Standard Operating Procedures for Semivolatile Organic Compounds in Dry Deposition Samples

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1.0 Overview

1.1 Tare weights and final weights of dry deposition plates are determined at the Illinois Institute of Technology (IIT).

1.2 Immediately after the final weight is determined at IIT, two to four deposition plates from each site during each sampling period will be placed into precleaned 120 mL wide-mouth amber bottles, capped, labeled and stored frozen in the dark until shipped overnight unfrozen to Rutgers University/University of Minnesota (RU/UMN) via Federal Express.

1.3 Upon receipt at RU/UMN, samples are again stored frozen in the dark until analyzed.

1.4 Storage of samples will be limited to about one to two years prior to extraction.

2.0 Sample Extraction at RU/UMN

2.1 General Notes

All laboratory glassware and utensils are washed with Alconox and rinsed with tap water, Milli-Q® water (Millipore) and acetone and baked overnight at 450°C. All equipment is wrapped in aluminum foil during storage in the laboratory. Only pesticide grade solvents (Baxter) and reagent grade solids are employed as required during analytical procedures. Whenever clean glassware is used, the aluminum foil is first removed and the glassware rinsed with dichloromethane (DCM) prior to use. If at all possible, glassware openings are re-covered with aluminum foil during usage to minimize exposure to laboratory air. At all transfer steps, sample codes and descriptions are similarly labeled on the next vial containing that sample. Thus, the same sample code is passed from the original sample bottle to the final vial containing the final extract for instrument injection and final archiving. All procedures and sample codes are similarly recorded in laboratory notebooks and instrument logbooks. Detailed records of daily laboratory progress with all pertinent observations must be noted in the laboratory notebook by the individual performing the analytical tasks.

2.2 Specific Procedure

2.2.1 Using forceps, place all deposition strips from an individual amber bottle, representing one site exposed for one sample cycle (≈ one month) or two to three month composites, into a clean 35 mL screw-top amber glass vial.

2.2.2 Rinse the original sample bottle with two 1 mL aliquots of DCM and add to the extraction vial.

2.2.3 With syringe(s), add an appropriate amount of analytical surrogate standards (3,5-dichlorobiphenyl [IUPAC #14], 2,3,5,6-tetrachlorobiphenyl [IUPAC #65], and 2,3,4,4',5,6-hexachlorobiphenyl [IUPAC #166] for PCBs and t-nonachlor; d_8-naphthalene, d_{10}-fluorene, d_{10}-fluoranthene and d_{12}-perylene for PAHs) to the extraction vial. (The subset of samples for atrazine analysis will be additionally spiked with the surrogate, terbutylazine).

2.2.4 Add ≈ 30 mL of DCM to the extraction vial to cover the greased deposition strips.

2.2.5 Place the extraction vials in an ultrasonic bath, sonicate for 30 min and store vials overnight in a freezer.

2.2.6 Transfer the DCM to another clean amber 35 mL vial with two 1 mL hexane (HEX) rinses of the extraction vial.

2.2.7 Concentrate the DCM extract to ≈1 mL under a gentle N_2 gas stream.

2.2.8 Meanwhile, add approximately 30 mL of HEX to the original extraction vial with the dry deposition strips, sonicate for 15 min., and store vials overnight in a freezer.

2.2.9 After the DCM fraction is blown down to ≈1 mL, add the HEX fraction to the DCM vial with two 1 mL HEX rinses of the original extraction vial.

2.2.10 Discard the original extraction vial or reclean.

2.2.11 Concentrate the HEX to ≈1 mL under a gentle N_2 gas stream.

2.2.12 The HEX sample is now ready for cleanup (unless selected for atrazine analysis).

2.3 If samples are selected for *atrazine analysis:*

2.3.1 General Notes: Since atrazine is *not* expected to be observed in most dry deposition samples, only a select set of samples will be analyzed for atrazine. These samples will primarily include the spring samples (April, May, June) when atrazine is most likely to be detected on atmospheric particles. Because atrazine may not be recovered from silica gel/alumina column during sample cleanup for PCBs and PAHs, samples selected for atrazine analysis will be analyzed prior to clean-up. For this subset of samples, the following steps apply immediately following Step 12 above (otherwise skip to Sample Cleanup below).

2.3.2 Specific Procedure

2.3.2.1 Using a syringe, add an appropriate amount of d_5-atrazine to the uncleaned sample (≈ 1 mL HEX in 35 mL amber vial) as internal quantification standard LIS).

2.3.2.2 Concentrate the HEX to ≈200-500 µL under gentle N_2 gas stream.

2.3.2.3 Transfer the extract to an autosampler vial with a 250 µL glass insert and cap.

2.3.2.4 Place the autosampler vials within an autosampler tray and analyze on an HP-5890 GC with an HP-5971A MSD using a 30 m DB-5, 0.25 mm i.d., 25 µm film thick glass capillary column (J&W Scientific). The MSD is operated in selective ion monitoring mode with at least one confirmation ion.

2.3.2.5 Record sample codes in the instrument logbook in the order in which they are injected.

2.3.2.6 After samples are injected, transfer the samples from the autosampler vial back to the original HEX vial with four to five complete HEX rinses (≈ 1-1.5 mL total) of the glass insert within the autosampler vial.

3.0 Sample Cleanup

3.1 General Notes

Concentrated samples will be cleaned up to remove the grease from the dry deposition plates and other potential chemical interferences prior to instrumental analysis, using a 0.5 cm i.d. x 20 cm glass column with a 50 mL glass reservoir on top. Usually, enough columns are assembled to clean an entire sample set or at least half of a sample set in the course of one day.

3.2 Specific Procedure

3.2.1 Secure glass column to ring stand using clamps, being careful not to break column.

3.2.2 Install teflon stop-cocks.

3.2.3 Place a small clean glasswool plug into bottom of column.

3.2.4 Add pinch (≈ 0.5 cm) of clean anhydrous Na_2SO_4 to column.

3.2.5 With stopcock open, rinse column with ≈5-10 mL of DCM, letting the column drain completely.

3.2.6 Rinse column with ≈5 mL HEX and let drain to top of Na_2SO_4.

3.2.7 Close stopcock and add ≈ 5 mL HEX.

3.2.8 Add ≈ 5 cm 3% deactivated silica gel as slurry in HEX while slowly letting HEX drain from column and while tapping the column with rubber hose to help silica gel settle evenly within column. Do NOT allow HEX to drain below level of silica gel. (Silica gel: reagent grade, 60-200 mesh, Baker, activated overnight at 200°C, deactivated with MilliQ water by weight and stored overnight prior to use within dessicator.)

3.2.9 Add another pinch of clean anhydrous Na_2SO_4 to top of silica gel in column.

3.2.10 Add ≈5 mL HEX to column.

3.2.11 Add ≈ 5 cm 5% deactivated alumina (as dry solid) while slowly letting HEX drain from column and while tapping the column with rubber hose to help alumina settle evenly within column. Do not allow HEX to drain below level of alumina. (Alumina: neutral Brockman activity 1, 60-325 mesh, Fisher Scientific, activated overnight at 450°C, deactivated with MilliQ water by weight and stored overnight prior to use within dessicator).

3.2.12 Add ≈0.5 cm clean anhydrous Na_2SO_4 to top of column.

3.2.13 Add ≈10 mL HEX to clean and condition column and let drain to top of Na_2SO_4.

3.2.14 Place 25 mL amber vial beneath column. This vial must be labeled with same sample code as on sample vial to be cleaned.

3.2.15 Add sample extract to top of column and drain solvent to top of column while collecting eluant in vial. At no time allow solvent to drain beyond level of Na_2SO_4 at top of column.

3.2.16 When HEX reaches top of column, add two 1 mL HEX rinses of sample vial.

3.2.17 Again, when HEX reaches top of column, add 5 mL HEX to top of column and let drain to top of column.

3.2.18 When HEX reaches top of column, add 9 mL 1:4 DCM:HEX (v/v) and collect eluant in the same 25 mL amber vial as above.

3.2.19 When DCM:HEX drains completely from column, cleanup is complete.

3.2.20 Concentrate eluant to ≈ 1 mL under gentle N_2 gas stream.

3.2.21 Transfer sample to a 4 mL amber vial with ≈ 2-1 mL HEX rinses of 25 mL vial.

3.2.22 With syringe(s), add appropriate amounts of internal quantification standards (2,4,6-trichlorobiphenyl [IUPAC #30] and 2,2',3,4,4',5,6,6'-octachlorobiphenyl [IUPAC #204] for PCBs and t-nonachlor; and d_{10}-acenaphthalene, d_{10}-phenanthrene, d_{10}-pyrene, d_{12}-benzo(e)pyrene and d_{12}-benzo(g,h,i)perylene) for PAHs.

3.2.23 Concentrate the final extract ≈25-100 µL under gentle N_2 gas stream prior to injection on GC-ECD (PCBs and t-nonachlor) or GC-MSD (PAHs).